Fluid Phase Equilibria

Liquid-Liquid Coexistence Curves with Three Critical Points: 2-Butanol/Water System[1]

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[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.

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Key words: liquid-liquid equilibria, mixture, coexistence curve, three critical points, method of calculation, 2-butanol/water system.

ABSTRACT

In accord with the literature data only the closed loop coexistence curves for the 2-butanol/water system have been observed experimentally under the elevated pressures. However, the shape of the liquid-liquid coexistence curve at atmospheric pressure could be interpreted as the existence of the third critical consolute point. The thermodynamic analysis of coexistence curves with any number of critical consolute points was fulfilled for the system. The properties of three critical point coexistence curves reflecting the interconnection between conjugate temperatures were applied to describe mutual solubility evolution of the 2-butanol/water system with pressure. The position of an immiscibility gap with the third (upper) critical point at low temperatures was calculated for the 2-butanol/water system on the basis of the experimental literature data. Pressure dependencies of critical parameters (critical temperatures, critical concentrations) and general parameters of interaction energy were discussed. The position of a hypercritical point was compared with the literature data, and the positions of a critical double point and critical triple point were estimated. A novel way to represent data on the universal scale was proposed and demonstrated.

INTRODUCTION

Some systems exhibit a multiply reentrant solubility [1]. Phase-separating systems with two critical points (CPs) have been studied experimentally: closed-loop coexistence curves (CCs) [2-6] or two independent phase-separating domains [7], when the temperature of the lower critical solution point (LCSP) is above the temperature of the upper one (UCSP) have been observed.

Although a set of experimental data for the systems with three CPs is solely limited, it does straightforwardly confirm the existence of phase diagrams of this kind. The most impressive results have been presented in the paper of Sorensen [8], where the evolution of immiscibility gaps had been obtained in the 2-butanol/water system with the varied concentration of the third component (tret-butanol). However, for a binary 2-butanol/water mixture only the closed-loop coexistence curves have been observed experimentally. The data presented in [9] could be mentioned as a classical example of the variations in the closed-loop CCs for the 2-butanol/water system with the pressure.

The dependence of the CC shape on pressure near CP has been investigated thoroughly in [10] and the parameters of the critical double point (CDP) have been obtained: T_{CDP} = 274.15 ^{0}K and p_{CDP} = 10.07 MPa. However, in both papers the data on the low-temperature CC with UCSP were missing.

There exist the data of Dolgolenko [11] (Fig.1) which show the aqueous solutions of different fractions of 2-butanol have quite different phase diagrams at atmospheric pressure, namely, the purer is 2-butanol, the larger is the gap of immiscibility with one UCSP. Moreover, the shape of the phase-separation diagram for the purest 2-butanol should be interpreted as the existence of three critical consolute points. On the

one hand, the comparison with Sorensen data [8] shows that the largest immiscibility gap with one UCSP (fraction C) corresponds to a decreased amount or even the absence of tret-butanol. The first fractions of 2-butanol (fraction A) can be enriched with higher alcohol yielding a closed-loop located above the unclosed immiscibility gap with UCSP. On the other hand, the comparison with Moriyoshi et al. data [9] shows that at atmospheric pressure both Dolgolenko [11] and Moriyoshi et al. [9] phase-separation diagrams for the purest 2-butanol agree very closely. This fact indicates the necessity of existence of the third CP at low temperatures in the 2-butanol/water system. On increasing pressure one can expect an appearance of a closed-loop CC which degenerates into a hypercritical point (HCP), if two of CPs merge. The shape of CC at low pressure indicates the system transition over CDP in the vicinity of 100 atm: the closed-loop and the immiscibility gap with UCSP at low temperatures coincide in CDP.

The goal of the present work is to analyse a variety of the immiscibility phase diagrams existing in literature for the 2-butanol/water system as a system with three CPs, to formulate the conditions of continuous transition from one CP to the other, and to illustrate new properties of the CCs with three CPs. In particular, we attempt to obtain the data on solubility of the 2-butanol/water system (system with three CPs) in the low-temperature region using the properties of conjugate temperatures.

GENERAL EQUATIONS AND PROPERTIES

There is an uncertainty in description of the critical state for the systems with several CPs, i.e. when the system nears one of the critical points it recedes from the others. The limitation of usage of a simple scaling equations for description CCs over a broad interval of thermodynamic parameters variations does not allow one to consider a

phase diagram with several CPs as a solution of a unique equation. On the other hand, both microscopic [12] and phenomenological [13] approaches describe CCs with several CPs only qualitatively because of the nonclassical behaviour of the system in the vicinity of CPs. We have analysed the coexistence curves with any number of critical consolute points on the basis of the extended thermodynamic theory of regular mixing [14].

The asymmetry of CC is another difficulty in a unified description of the shape of CC. The principles of CC symmetrization which we employ in this paper have been considered elsewhere [15,16]. In brief, the connection between the mole ratios of initial components (X) and symmetric coordinates (X_s) is expressed by the formula:

$$X_S = (X - X_0)/(X_c - X_0) \qquad (1)$$

The fitting parameters X_c and X_0 are calculated by means of the least-mean square procedure using the properties of a symmetrized coexistence curve.

As we have already considered the issues of coexistence curve asymmetry, in further description we deal with the symmetric phase diagrams.

The excess Gibbs free energy of mixing in the frame of the symmetric regular-mixing model can be expressed as follows [17-19]: $G_e = \Delta H - T(\Delta S_1 + \Delta S_2)$, where $\Delta S_1 = -R[x_s \ln(x_s) + (1 - x_s)\ln(1 - x_s)]$ is the configurational molar entropy of mixing, $\Delta S_2 = x_s(1 - x_s)W_S$ is the molar excess entropy of mixing, arising from changes in the internal degrees of freedom upon mixing, $\Delta H = x_s(1 - x_s)W_H$ is the excess molar enthalpy of mixing.

Equation of CC (binodal) is determined under the condition $\partial G_e / \partial x_s = 0$:

$$X_S = \exp\left(\frac{X_S - 1}{X_S + 1}\frac{W_G}{RT}\right), \qquad (2a)$$

and the boundary of metastable states (spinodal) is determined under the condition $\partial^2 G_e / \partial^2 x_s = 0$:

$$\mathrm{X_S} = 2x_s W_G / RT, \qquad (2b)$$

where $W_G = W_H - TW_S$ is the general interaction energy parameter expressed in units of free energy. Critical temperature is found from the extremum conditions coincided for both curves, Eqs.(2). If the system under study has n CPs, the real positive roots of the following equation $W_G(\mathrm{T}, \mathrm{T_{ci}}) = W_H - T_{ci} W_S = 2RT_{ci}$ yield n critical temperatures $\mathrm{T_{ci}}$. $\mathrm{W_G}$ can be expressed in the universal form, assuming $W_S = \sum_{i=1}^{n} W_{Si} T^{i-1}$:

$$W_G = 2RT^* + W_{S1}(T^* - T), \qquad (3)$$

where $T^* = f(T, \{T_{ci}\})$ is the current critical temperature, which is a function of T and $\mathrm{T_{ci}}$ and near CP it goes to $\mathrm{T_{ci}}$. For the system with three CPs $T^* = [T_{c1}T_{c2}T_{c3} + T^2(T_{c1} + T_{c2} + T_{c3}) - T^3] / (T_{c1}T_{c2} + T_{c1}T_{c3} + T_{c2}T_{c3})$.

The equation of CC with any number of CPs has the following form

$$T = T^* \frac{W_{S1} + 2R}{W_{S1} + K_W R}, \qquad (4)$$

where $\mathrm{K_W} = \frac{X_S + 1}{X_S - 1} \ln(X_S)$, $\mathrm{W_{S1}}$ is the only fitting parameter.

For the system with three CPs an equation for critical temperatures has the form of an algebraic equation of the third degree

$$[T_{\mathrm{ci}} + W_{\mathrm{S2}} / (3W_{\mathrm{S3}})]^3 + 3u[T_{\mathrm{ci}} + W_{\mathrm{S2}} / (3W_{\mathrm{S3}})] + 2q = 0, \qquad (5)$$

where $u = (W_{\mathrm{S1}} + 2R) / 3W_{\mathrm{S3}} - (W_{\mathrm{S2}} / 3W_{\mathrm{S3}})^2$,

$q = (W_{\mathrm{S2}} / 3W_{\mathrm{S3}})^3 - (W_{\mathrm{S2}} / 3W_{\mathrm{S3}})(W_{\mathrm{S1}} + 2R) / 2W_{\mathrm{S3}} - W_{\mathrm{H}} / 2W_{\mathrm{S3}}$.

The number of real solutions of the Eq.(5) depends on the determinant sign $D = u^3 + q^2$:

(i) if D > 0, there exists the only real root; herein $W_{S3} > 0$ corresponds to LCSP and $W_{S3} < 0$ corresponds to UCSP.

(ii) if D < 0, there are three real roots. Herein at $W_{S3} > 0$ the closed immiscibility gap is observed above the unclosed CC with UCSP, i.e. $T_{HCP} > T_{CDP}$. In Fig.2a one can see changes of the diagrams shape with increase of absolute value of positive W_H: large domain of immiscibility (1, 2) with one UCSP transforms into the closed-loop two-phase region located upper than the second domain of limited solubility, the CDP (3') is formed when LCSP of the closed-loop comes into contact with UCSP of unclosed CC; and then the closed-loop immiscibility gap (4) decreases up to shrinking into HCP (5'), and under further increase in the W_H only unclosed CC with UCSP (5, 6) is observed. Similar phase diagrams have been experimentally obtained [8] for the mixture of 3-butanol/2-butanol/water when the content of tret-butanol was sequentially increased. Behaviour of this type was described under studying phase diagrams of the 2-butanol/water solutions at elevated pressure [9].

At $W_{S3} < 0$ the reversed pattern is observed, namely: the closed-loop lies beneath the unclosed CC with LCSP. In Fig.2b one can see changes of the shape of CCs with three CPs when absolute but negative value of W_H is increased. Herein CDP (2') is a point of contact of UCSP of closed-loop and LCSP of the independent domain of immiscibility whereas HCP (4') is a point of degeneration of the closed-loop. In this case $T_{CDP} > T_{HCP}$. Finally, at large negative values of W_H a single unclosed CC with LCSP (5) is observed. In the literature we could not find any experimental data for transitions of this type.

(iii) if D = 0 ($u^3 = -q^2 \neq 0$) two CPs are coalesced forming either HCP or CDP at the temperature $T_D = -W_{S2}/(3W_{S3}) \pm \sqrt{-u}$.

(iv) if D = 0 (u = q = 0), then three CPs are coalesced, and the corresponding temperature is indicated as a critical triple point (CTP) $T_{CTP} = -W_{S2}/(3W_{S3}) = (T_{c1} + T_{c2} + T_{c3})/3$. The possibility of this case is evident from the analysis carried out (see Fig.2c).

Coefficients and roots of the Eq.(5) are related to each other as shown below:

$$\begin{cases} T_{c1} + T_{c2} + T_{c3} = -W_{S2}/W_{S3} \\ T_{c1}^{-1} + T_{c2}^{-1} + T_{c3}^{-1} = (W_{S1} + 2R)/W_H = T_0^{-1}, \\ T_{c1}T_{c2}T_{c3} = W_H/W_{S3} \end{cases} \quad (6)$$

where $T_0^{-1} = T_{c1}^{-1} + T_{c2}^{-1} + \cdots + T_{cn}^{-1} = const$. It follows from Eqs.(5) and (4) that critical temperatures T_{ci} and conjugate temperatures T', T" and T"' (temperatures at the same concentration) have to be associated to each other

$$\begin{cases} T' + T'' + T''' = T_{c1} + T_{c2} + T_{c3} = 3T_{CTP} \\ T'T'' + T''T''' + T'T''' = (T_{c1}T_{c2} + T_{c2}T_{c3} + T_{c1}T_{c3})(W_{S1} + K_W R)/(W_{S1} + 2R) \\ T'T''T''' = T_{c1}T_{c2}T_{c3} \end{cases} \quad (7)$$

and if the critical temperatures T_{ci} and one of the conjugate temperatures are known, the rest two conjugate temperatures can be calculated from Eqs.(7).

A program (SYSNEW) for numeric calculations of fitting parameters of the CC equation using experimental data has been created. The program has been described elsewhere in detail [20]. Here we just point out the features of the program: (a) the multidimensional optimisation has been realised, (b) the experimental data on liquid-liquid equilibrium taken from literature can be represented in the universal concentration coordinates (mole fractions, weight fractions, volume fractions, density, refractive index, and so on), (c) sequential (x_j, T_j) or conjugate (x_j', x_j'', T_i) experimental data can be used,

(d) any fitting parameter can be either frozen or calculated by least-mean square or iteration method, (e) to estimate quickly and illustratively the physical meaning of fitting parameters calculated, the interpolating functions are graphically compared with the experimental data.

RESULTS AND DISCUSSIONS

Using Eq.(7) and the data of Dolgolenko [11] with the available experimental points in the range of low temperatures for three conjugate temperatures, the position of a critical triple point was calculated: T_{CTP} = 306.14 ^{0}K. Further, assuming the position of this point unchanged under pressure variations, the upper critical solution temperatures in the range of low temperatures were evaluated for the Morioyshi et al. data [9] at higher pressures. These results are shown in Table 1 (column 3).

Calculating the symmetrized concentration parameters (x_c, X_0) we assume that critical concentrations for UCSP and LCSP are equal to each other. The basis for this assumption has been discussed in [15,16]. We obtained that parameter X_0 was zero for all pressures while the critical concentrations x_c were slightly changed with pressure (Table 1, column 7). However, within the experimental errors these changes are negligible and the values could be considered as constant.

The energy parameters (T_{ci}, B) were calculated independently for symmetrized CCs under fixed exponent σ = 0.325 of the scaling law of W_{S1} variation: $W_{S1} = B\tau_0^{-\sigma}$, where $\tau_0 = (T^* - T)/T_0$. The accuracy of the data for the studied systems was not sufficient to evaluate the value of σ. In our calculations we used the value of σ previously obtained [21] using the more precise data for the methanol/heptane system [22].

The position of HCP, CDP, and CTP can be evaluated from the condition D = 0.

The temperatures of HCP and CDP (T_{D1} and T_{D2}) associate with critical temperatures T_{ci} and the temperature of CTP, T_{CTP}:

$$\begin{cases}(T_{D1}+T_{D2})/2=(T_{c1}+T_{c2}+T_{c3})/3\\ T_{D1}T_{D2}=(T_{c1}T_{c2}+T_{c2}T_{c3}+T_{c1}T_{c3})/3\end{cases} \quad (8)$$

The calculated values of T_{D1} and T_{D2} are presented in Table 1 (columns 7 and 8) for different pressures. It is clear that T_{D1} and T_{D2} are slightly changed with pressure. These data were used to calculate the coexistence curves and critical parameters for the cases of 1 atm and 100 atm pressure because, as it is shown in Fig.2a (curves 1,2,3), the system has the only CP and two overlapping immiscibility gaps.

The calculation of limiting temperatures for HCP and CDP was based on the following considerations. In the case of HCP the critical temperatures of the closed-loop CC become equal, and in the case of CDP one critical temperature of an unclosed CC coincides with one of the critical point of a closed-loop. In both cases the equations to determine these characteristic critical temperatures are identical

$$\begin{cases}T_c+2T_D=3T_{CTP}\\ 2T_D^{-1}+T_c^{-1}=T_0^{-1}\end{cases}, \quad (9)$$

here T_D is either T_{HCP} or T_{CDP}, T_c is one of the rest critical points. Using Eq.(9) we calculated the temperatures for both HCP and CDP and the correspondent UCSP: 1) T_{HCP} = 339.84 K and T_c = 238.74 K (p_{HCP} = 845 atm), this case corresponds to the Fig.2a (5',5); 2) T_{CDP} = 268.27 K and T_c = 381.87 K (p_{CDP} = 100 atm), this case corresponds to the Fig.2a (3',3). The values are in good agreement with the literature data. The position of CDP and correspondent UCSP are coincided with those for characteristic points obtained for the data of Moriyoshi et al. at p = 100 atm. This pressure is very close to the value of CDP p_c = 10.07 MPa obtained in [10] for the 2-butanol/water system.

Finally, the possibility of quantitative description of the phase diagrams with three critical points at different pressures is shown in Fig.3. The calculated parameters of CCs are presented in Table 1.

The obtained critical temperatures allowed us to calculate the so-called compensation temperature T_0, which appears to be constant with good precision for all pressures (see Table 1, column 9).

A critical line connecting the critical solution points as miscibility limits can be obtained from the results presented in Table 1, and shown as the (p,T)-projection in Fig.4. This plot includes the low-temperature part located below the CDP, where the measurements of the critical point and the solubility temperatures are experimentally difficult. Parts 1 and 3 of the critical point line can be described by the formulae [23]

$$T_{ci} - T_D = \pm l_1 (p - p_D)^{1/2} + l_2 (p - p_D), \qquad (10)$$

where T_{ci} is the single critical temperature at pressure p, "+" applies for $T_{ci} > T_D$, l_i's are the fitted coefficients, and D indicates either CDP or HCP. Calculated fitting parameters are $l_1 = 1.32 \pm 0.03$ and $l_2 = 0.004 \pm 0.001$. The intermediate part 2 is significantly affected by both HCP and CDP. We used the sum of the Eq.(10) with different signs to describe the critical line between HCP and CDP:

$$T_{ci} = (T_{CDP} + T_{HCP})/2 + l_1[(p - p_{CDP})^{1/2} - (p - p_{HCP})^{1/2}] + l_2[(p - p_{CDP}) + (p - p_{HCP})] \qquad (11)$$

Here p_{CDP} = 100 atm, p_{HCP} = 845 atm. Interestingly, that in both equations (10) and (11) the same fitting parameters were used for approximation of the whole critical line.

The value of critical amplitude B for different pressures varies within the experimental errors that are shown in Table 1, column 5. It means that we cannot recognise a difference in the critical amplitudes B for these data, and we have to take average B,

which is the same for all pressures, indicating that there are no changes in the internal degrees of freedom. This calculated average B = 22 ± 7 was used for the unique description of the analysed data. To clarify the variations of the CC's shape with pressure the universal scale, the reduced temperature of phase separation, T/T^*, versus symmetrized mole fraction, x_s, can be used. The reduced CCs with three CPs were theoretically calculated under the constant value of the critical amplitude B for the same pressures indicated in Fig.3. These results are presented in Fig.5. It should be emphasised that even if the whole dependence is described by the same equation with equal critical amplitude B for all pressures, the curve does contain two different lines corresponding to the closed-loop region (solid line) and unclosed immiscibility gap (shot dotted line). At p = 1 atm (Fig.5a) both lines are connected below the point $T/T^* = 1$, i.e. there are no closed-loop gaps. One can compare this curve with Fig.3a. Fig.5b shows the case of CDP (see Fig.3b): the closed-loop region (solid line) is maximal. With increasing the pressure (compare Fig.5c and d with Fig.3c and d, respectively) the closed-loop regions (solid lines) became more and more narrow shrinking into the point when the HCP is reached. For all pressures reverse point (A) corresponds to the same temperature T_{HCP} = 339.84 K, but different concentrations and different T/T^*.

CONCLUSION

The data of Moriyoshi et al. [9] for the 2-butanol/water system at different pressure has been analysed as a system with three critical points. The experimental liquid-liquid equilibrium data of different authors provide a basis for considerations of this sort. We used the general properties of conjugate temperatures of CCs with several CPs to calculate the low-temperature part of the whole CC. This is especially important in

connection with the difficulties of experimental measurements in this region. Moreover, a quantitative picture of complex topology phase diagrams of this type has allowed us to understand fine features of solubility curves with several CPs. The comparison of CCs for the system with three CPs on the universal concentration and energy scale can be regarded as a development of the principle of corresponding states. The generalized approach allows us to include the systems of different physico-chemical nature and ternary mixtures in the unique scheme of quantitative description of solubility phase diagrams. The program used for the CCs calculation is a basis for creation a computer databases on the liquid-liquid equilibrium which replenishment is being continued.

List of symbols

B	critical amplitude of the CC
R	gas constant
T	absolute temperature
T*	current critical temperature
T_{ci}	single critical temperature
T_0	enthalpy-entropy compensation temperature
W_G	$= W_H - T W_S$, general interaction energy parameter
x	mole fraction (mol.fr.) of component A (solvent)
X	$= x/(1-x)$, mole ratio of initial components
x_c	critical mol.fr. of component A
X_c	$= x_c/(1-x_c)$, mole ratio of initial components
x_0	limit mol.fr. of isotropic solution
X_0	$= x_0 /(1-x_0)$
x_s	symmetrized mol.fr. of component A
X_s	$= x_s/(1-x_s)$
σ	critical exponent of the scaling law of W_{S1} variation
τ_o	general reduced temperature.
τ_i	$= (T-T_{ci})/T_{ci}$, reduced temperature

REFERENCES

[1] J.S.Walker and Ch.A.Vause, Scientific Amer., 256 (1987) 98-105.

[2] B.Ch.McEwan, J. Chem. Soc., 123 (1923) 2284-2288.

[3] H.L.Cox, W.L.Nelson, L.H.Cretcher, J. Am. Chem. Soc., 49 (1927) 1080-1083.

[4] H.L.Cox and L.H.Cretcher, J. Am. Chem. Soc., 48 (1926) 451-453.

[5] C.S.Hadson, Z. Phys. Chem., 47 (1904) 113-115.

[6] K.Ochi, M.Tada, K.Kojima, Fluid Phase Equilibria, 56 (1990) 341-459.

[7] H.R.Kruyt, Ann. Chim. Phys., 31 (1908) 486-510.

[8] C.M.Sorensen, Int. J. Thermophys., 9 (1988) 703-712.

[9] T.Moriyoshi, S.Kaneshina, K.Aihara, K.Vabumoto, J. Chem. Thermodyn., 7 (1975) 537-545.

[10] F.Monroy, A.G.Casielles, A.G.Aizpiri, R.G.Rubio, F.Ortega, Phys.Rev.B, 47 (1993) 630-637.

[11] W.Dolgolenko Z. Phys. Chem., 62 (1908) 499-511.

[12] J.S.Walker, F.Ghebremichael, Pure & Appl. Chem., 63 (1991) 1381-1386.

[13] R.E.Goldstain, J. Chem. Phys., 83 (1985) 1246-1254.

[14] S.V.Kazakov, O.P.Revokatov, N.I.Chernova, Doklady Physics, 43 (1998) 137-140.

[15] S.V.Kazakov, N.I.Chernova, Rus. J. Phys. Chem., 69 (1995) 1010-1014.

[16] S.V.Kazakov, N.I.Chernova, Rus. J. Phys. Chem., 71 (1997) 234-239.

[17] I.Prigogine and R.Defay, Chemical Thermodynamics, Longmans Green and Co, London-New York-Toronto, 1954.

[18] J.B.Thompson, Jr., Researches in Geochemistry, 2 (1967) 340-361.

[19] J.H.Hildebrand, J.M.Prausnitz, R.L.Scott, Regular and related solutions. The solubility of gases, liquids, and solids, Van Nostrand Reinhold Co., N.Y., 1970.

[20] S.V.Kazakov, Thesis (D.Sc.), Kurchatov Nuclear Physics Institute., Moscow, 1998.

[21] S.V.Kazakov and N.I.Chernova, Proc. 4th Thermophys.Prop.Conf., Tokyo, D3d6 (1995) 841-845.

[22] A.G.Aizpiri, J.A.Correa, R.G.Rubio, M.D.Pena, Phys.Rev.B, 41 (1990) 9003-9012.

[23] N.P.Malomuzh, B.A.Veytsman, Physica A, 168 (1990) 833-852.

Table 1. Critical parameters of the 2-butanol/water system under different pressure.

Pressure, atm	T_{c1}/K	T_{c2}/K	T_{c3}/K	B	x_c	T_{D1}/K	T_{D2}/K	T_0/K
1	388.0	--	--	19 ± 9	0.124	268.27	345.0	--
100	381.6	268.27	268.27	21 ± 7	0.124	268.27	343.6	--
200	378.4	288.1	251.8	21 ± 9	0.124	268.4	343.8	99.2
300	373.2	297.0	248.3	23 ± 9	0.125	269.9	342.5	99.3
400	368.8	303.0	246.2	24 ± 5	0.125	270.6	341.4	99.3
500	364.6	309.2	244.5	25 ± 5	0.125	271.4	340.7	99.3
600	360.6	315.3	242.6	25 ± 7	0.125	271.8	340.5	99.3
700	356.5	322.4	240.0	23 ± 5	0.125	271.7	340.8	99.3
800	349.6	330.5	238.9	18 ± 5	0.126	272.1	340.5	99.3

FIGURE CAPTIONS

Fig.1. Solubility curves for the 2-butanol/water system at atmospheric pressure: the comparison of the data of Dolgolenko [11] and Moriyoshi et al. [9]. The calculated hypercritical (HCP), critical triple (CTP), and critical double (CDP) points are indicated in Figure.

Fig.2. Schematic representation of solubility phase diagrams with three CPs:

a) $T_{HCP}>T_{CDP}$, transition from UCSP (1) to UCSP (6) sequentially occurs over CDP (3') and HCP (5'): $W_{S3} = 10^{-4}R$, $W_{S2} = -0.09282R$, $W_{S1} = 26.3768$; (1) $W_H = 2876.1R$, (2) $W_H = 2866.1R$, (3) $W_H = 2863.796R$, (4) $W_H = 2860.1R$, (5) $W_H = 2848.419R$, (6) $W_H = 2836.1R$.

b) $T_{HCP}<T_{CDP}$, transition from LCSP (1) to LCSP (5) sequentially occurs over CDP (2') and HCP (4'): $W_{S3} = -10^{-4}R$, $W_{S2} = 0.09R$, $W_{S1} = -28.7$; (1) $W_H = -2590R$, (2) $W_H = -2603.68R$, (3) $W_H = -2610R$, (4) $W_H = -2616.325R$, (5) $W_H = -2630.1R$.

c) The coincidence of three CPs: $W_{S3} = 10^{-4}R$, $W_{S2} = -0.09R$; (1) $W_{S1} = 24.7$, $W_H = 2610R$; (2) $W_{S1} = 24.97$, $W_H = 2691R$; (3,3') $W_{S1} = 25.0$, $W_H = 2700R$. (3') is the critical triple point (CTP).

Fig.3. Solubility curves for the 2-butanol/water system at different pressures: a) 1 atm, b) 100 atm, c) 200 atm, d) 800 atm, where x and x_s are mole fraction and symmetrized mole fraction for 2-butanol, respectively. Points are the experimental data of (o) Dolgolenko [11] and (•) Moriyoshi et al. [9]. Lines are the initial (solid) and symmetrized (shot dotted) coexistence curves calculated using Eqs.(1)-(4) with the parameters presented in Table 1. The calculated hypercritical (HCP), critical triple (CTP), and critical double (CDP) points are indicated in Figure.

Fig.4. Pressure dependence of the critical solution temperatures. The solid circles corre-

spond to the experimentally reached domain, the open circles are located in the low-temperature part of solubility curves. The calculated hypercritical (HCP), critical double (CDP) points (⊗), and correspondent UCSPs (×) are indicated. Lines are calculated by Eqs.(10) and (11) with the same fitting parameters l_1 and l_2 (see in the text).

Fig.5. Comparison of symmetrized coexistence curves of the 2-butanol/water system at different pressures in reduced scale: the solid line corresponds to the closed-loop, the shot dotted line corresponds to the unclosed immiscibility gap, both lines are calculated using Eq.(4) with the parameters: $B = 22 \pm 7$, $\sigma = 0.325$,

a) 1 atm: $T_{CDP} = 268.27$ K, $T_{HCP} = 339.84$ K, $T_c = 388.0$ K,

b) 100 atm: $T_{CDP} = 268.27$ K, $T_{HCP} = 339.84$ K, $T_c = 381.55$ K,

c) 200 atm: $T_{c1} = 378.44$ K, $T_{c2} = 288.06$ K, $T_{c3} = 251.82$ K,

d) 800 atm: $T_{c1} = 349.55$ K, $T_{c2} = 330.45$ K, $T_{c3} = 238.86$ K.

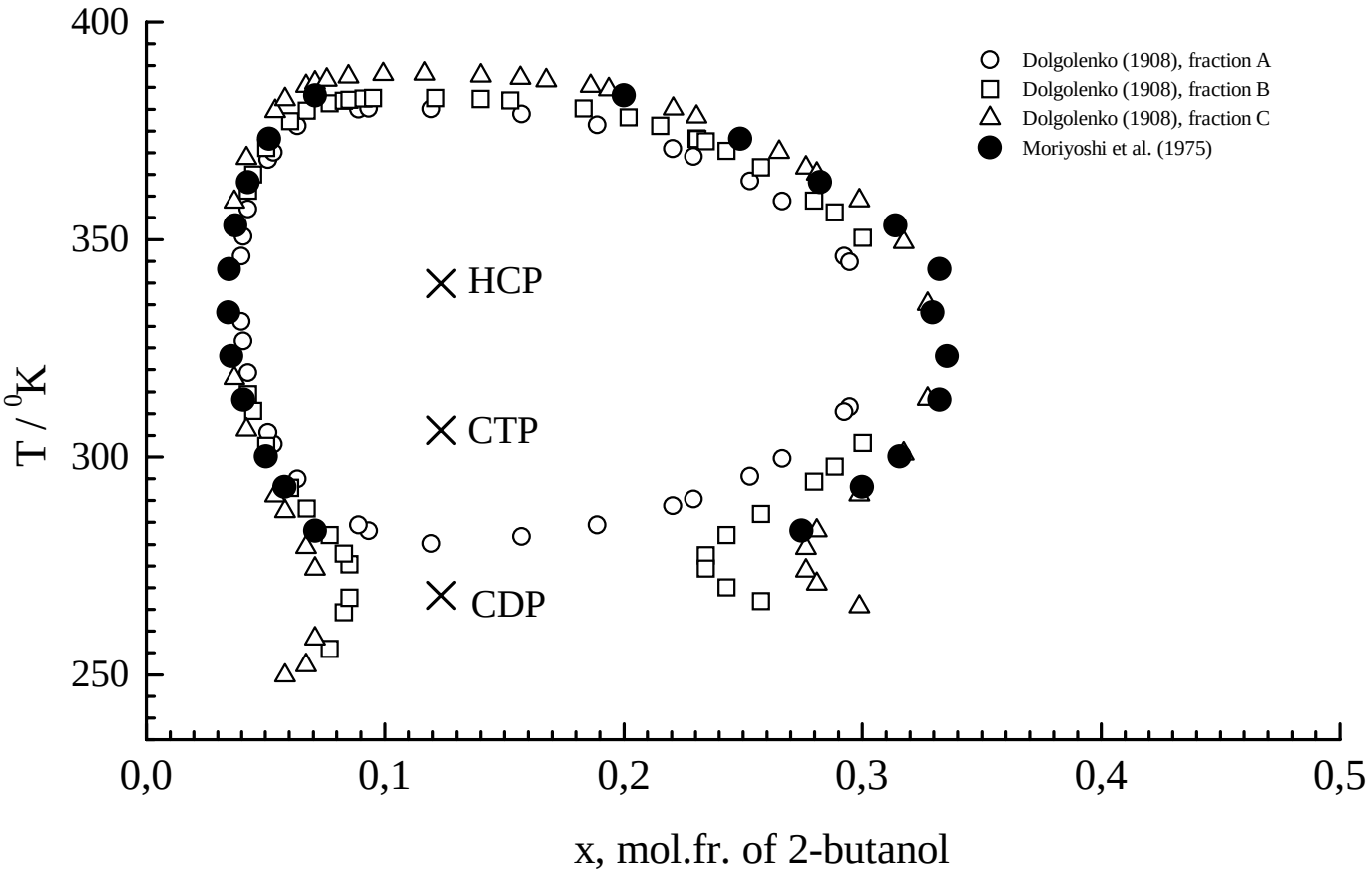

Fig.1. Kazakov and Chernova

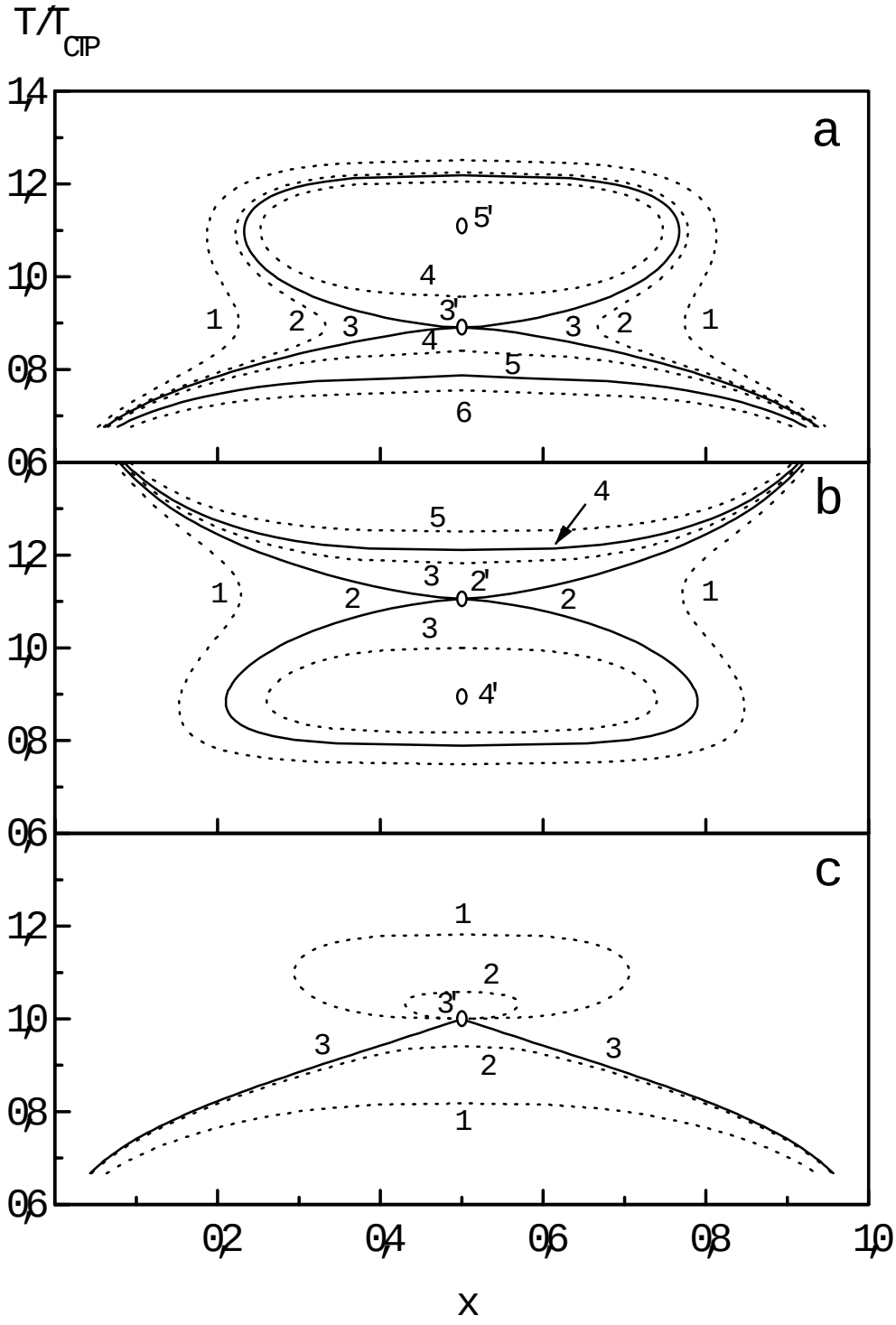

Fig.2. Kazakov, Chernova

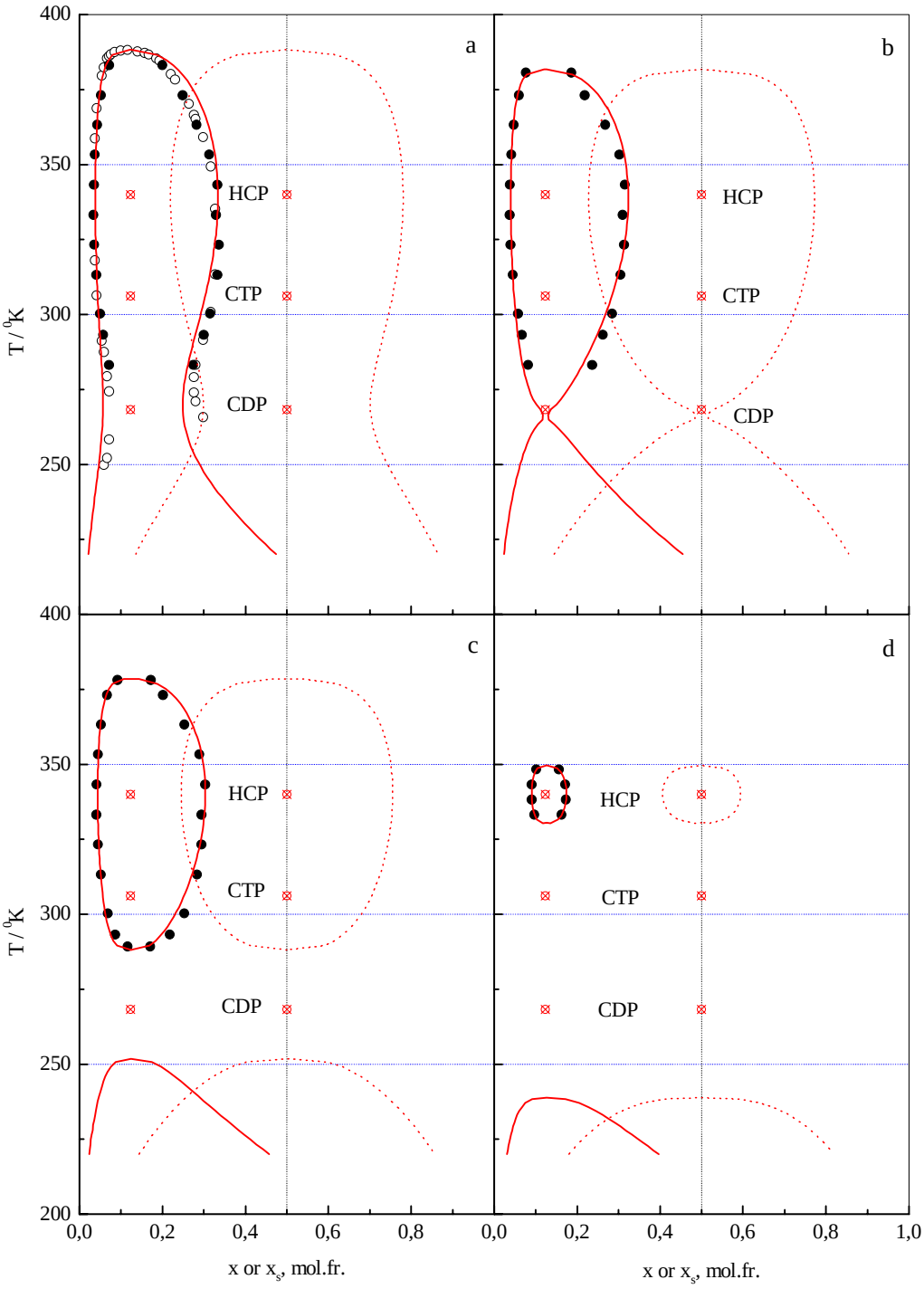

Fig.3. Kazakov and Chernova

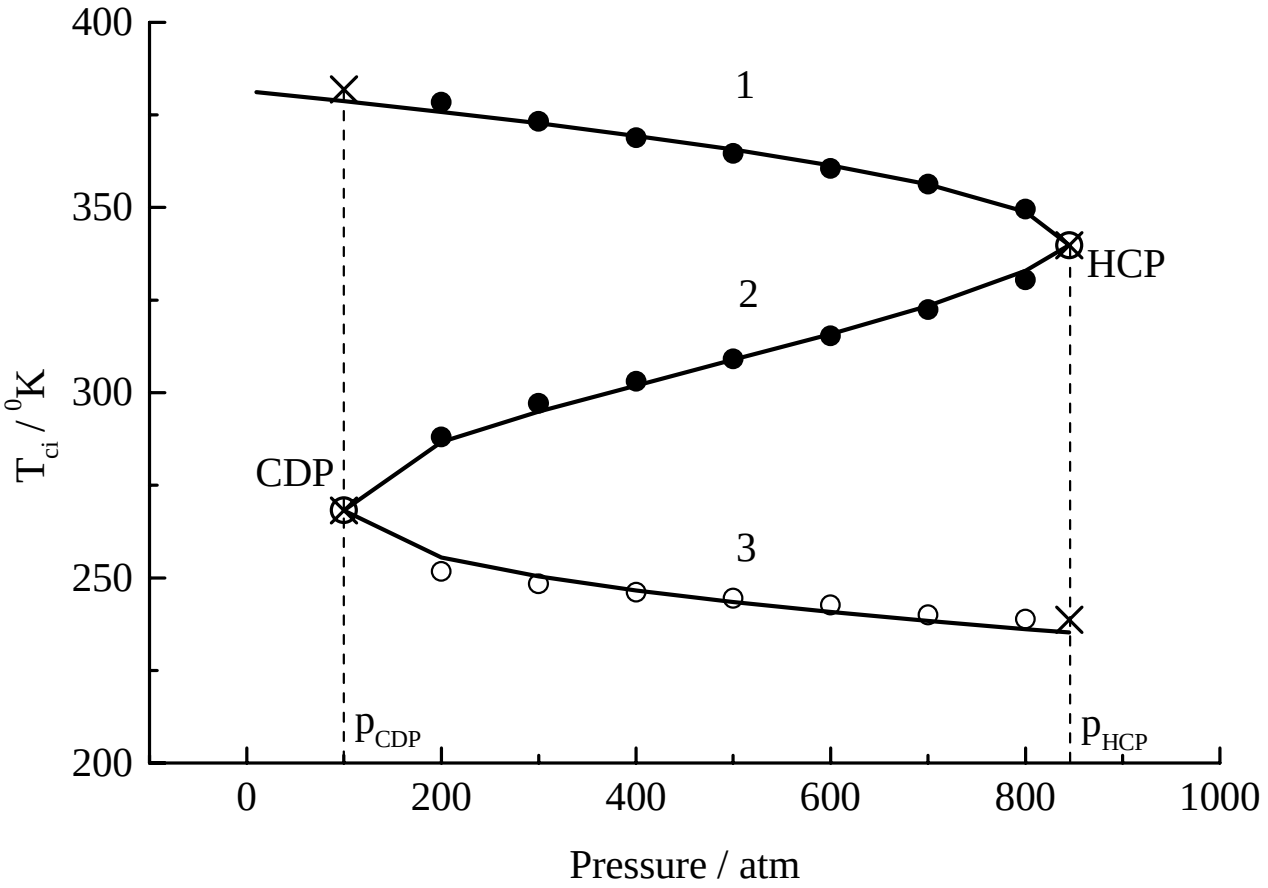

Fig.4. Kazakov and Chernova

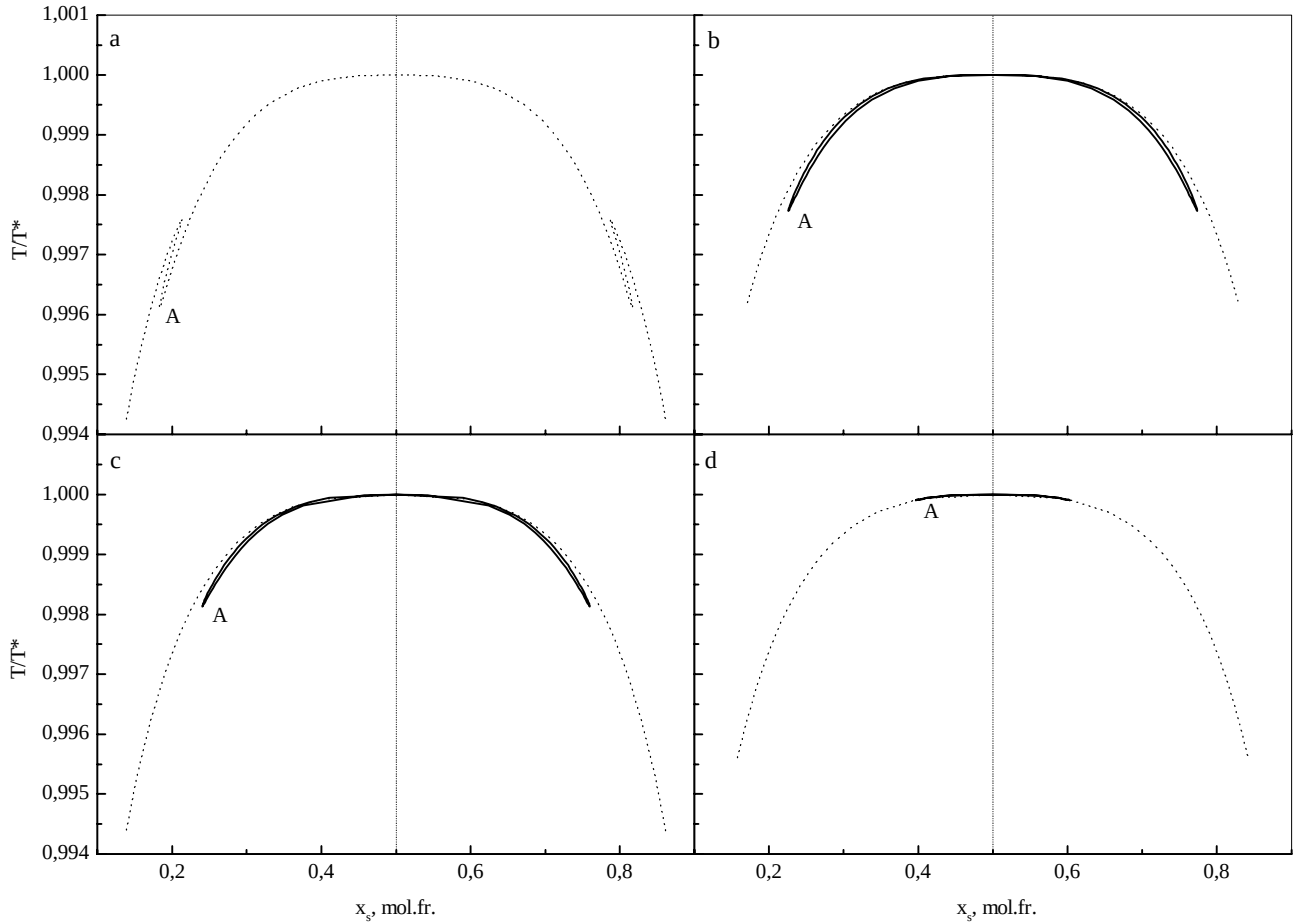

Fig.5. Kazakov and Chernova